

Air-stable naphthalene derivative-based electrolytes for sustainable aqueous flow batteries

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The growing global capacity for renewable energy generation necessitates the deployment of energy storage technologies with a combination of low cost, good performance and scalability. With these advantages, aqueous organic flow batteries have the potential to be the system of choice because they could store energy from organic redox-active molecules. Here we report naphthalene derivatives as organic redox-active molecules that exhibit high solubility (~1.5 M) and a stable redox-active framework with no obvious capacity decay over 40 days (50 Ah l⁻¹) in an air atmosphere in flow batteries. We report a battery that runs smoothly even under continuous airflow without obvious capacity decay for ~22 days (more than 600 cycles). A series of spectral analyses and theoretical calculations reveal that the dimethylamine scaffolds improve the water solubility and protect the active centre, ensuring the stability of the molecules during the charge and discharge process. Owing to the success in kilogramme-scale molecular synthesis, pilot-scale stack expansion with notable cycling stability over 270 cycles (~27 days) is attained. The cost benefit evidenced by technoeconomic analysis together with the stability even under open-air conditions indicates the practical value of the present molecular system in grid-scale energy storage.

Flow batteries (FBs) have drawn considerable attention because of their ability to alleviate the instability and intermittence of renewable energy, owing to their independent power and capacity, safety, scalability and design flexibility^{1–3}. Among various FB types, aqueous organic flow batteries (AOFBs) use naturally abundant, structurally diverse and synthetically tunable organic redox-active molecules (ORAMs) as redox species and have emerged as promising technologies for energy storage systems^{4–7}. To date, various ORAMs, including quinone-based molecules², heterocyclic aromatic molecules^{8,9}, 2,2,6,6-tetramethylpiperidine-1-oxyl derivatives^{10–12}, fluorenones^{7,13},

polymer-based molecules⁵ and metal complex compounds¹⁴ have been investigated for AOFBs; however, the stability of the molecular structure is a critical issue when designing ORAMs because side reactions such as nucleophilic reactions, disproportionation, irreversible tautomerization and dimerization can inactivate ORAMs, resulting in complete loss of their redox activity and capacity decay of AOFBs^{15–17}. For example, some types of ORAMs are susceptible to nucleophilic attack by H₂O (through the Michael reaction), resulting in irreversible structural transformation; this exposure to H₂O is inevitable in AOFBs because of the presence of a large amount of water^{16,18,19}. To improve

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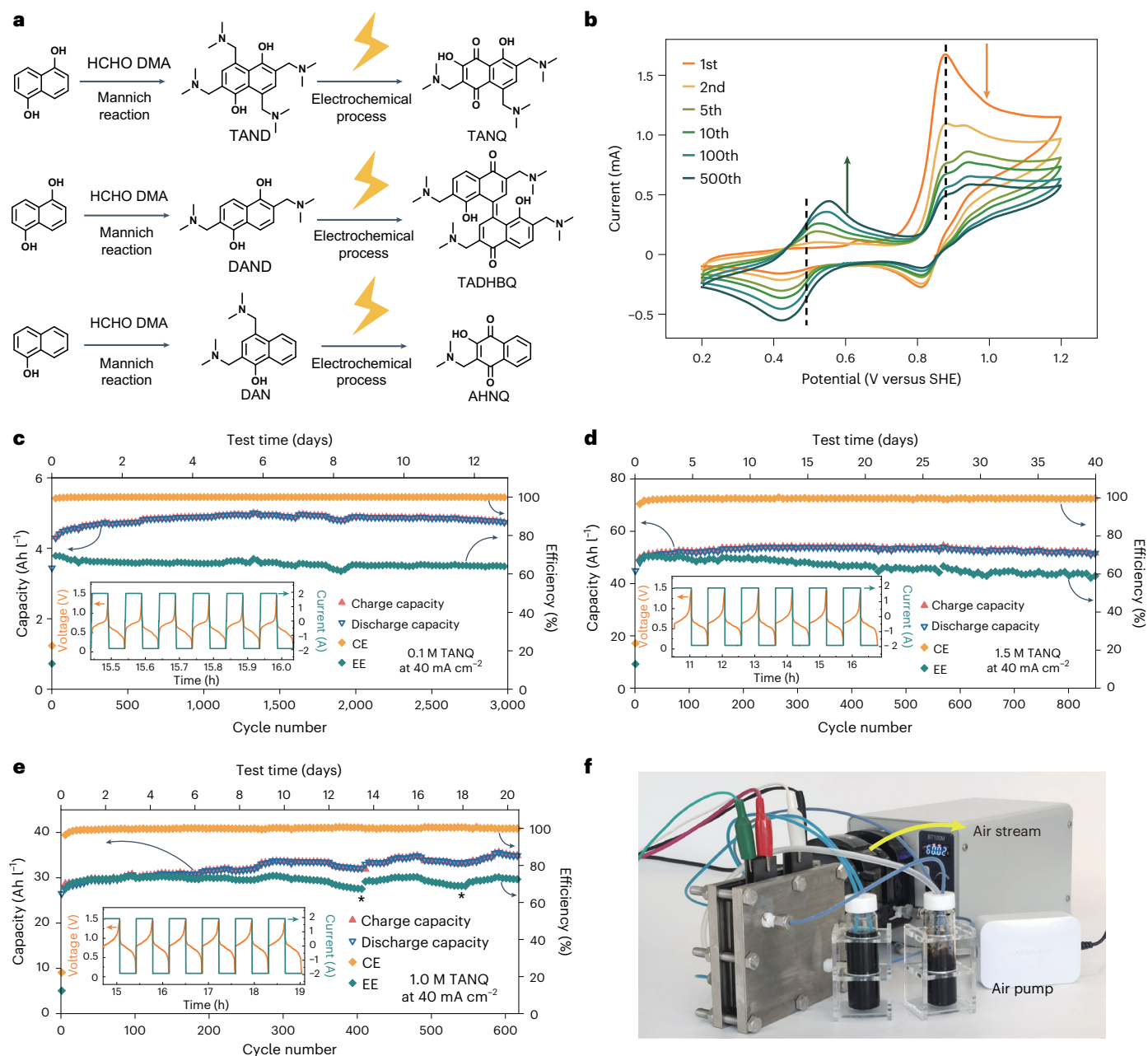


Fig. 1 | Chemical and electrochemical reaction and battery performance of naphthalene derivatives. **a**, Chemical and electrochemical reaction of the naphthalene derivatives from hydroxynaphthalene to TANQ, TADHBQ and AHNQ. **b**, CV with 10 mM TANQ in 3 M H₂SO₄ solution (scan rate, 50 mV s⁻¹). The black vertical dashed lines in CV curves represent the formal potential of TANQ/TADHBQ (reversible peaks) and oxidation potentials of TAND during electrochemical oxidation (irreversible peaks). **c**, Long-term cycling capacity and efficiencies of a 0.1 M TANQ-based AOFB with an SWO anolyte. **d**, Long-term cycling capacity and efficiencies of a 1.5 M TANQ-based catholyte AOFB with an SWO anolyte. **e**, Long-term capacity and efficiencies under air-bubbling

conditions of an FB containing a 1.0 M TANQ-based catholyte and a 1 M vanadium anolyte. The insets in **c–e** represent the corresponding charge–discharge profiles. The solvent continuously evaporated as the air was incessantly constantly pumped into the positive reservoir, and additional solvent was added to the catholyte (denoted by the asterisks) to ensure an appropriate amount of electrolyte. **f**, Air-bubbling test of an FB containing a 1.0 M TANQ-based catholyte and a 1.0 M vanadium anolyte. Air was continuously pumped into the catholyte by an external air pump to further confirm the durability of the naphthalene-based catholyte when thoroughly exposed to an air atmosphere (20 ml min⁻¹). SHE, standard hydrogen electrode. DMA, dimethylamine.

ORAM reliability and extend the FB lifespan, molecular engineering has been employed to increase structural stability^{4,10}. The redox reversibility of ORAMs is highly dependent on the types and positions of functional groups and the extension of the aromatic structure^{20–22}.

Moreover, air stability remains a critical challenge for most reported ORAMs since their reduced states are generally sensitive to air and can easily react with dissolved O₂ and singlet O or peroxide. This results in ORAM oxidation and other irreversible side reactions, thus

leading to FB capacity decay^{23,24}. For example, the rate constant for the reaction of reduced methyl viologen with O₂ reaches 10⁹ M⁻¹s⁻¹, and ferrocenium (Fc⁺) reacts with oxygen to produce an unstable dimeric complex that further decomposes into inactive species^{25–27}. Polycyclic aromatic hydrocarbon derivatives, such as naphthalene, phenanthrene and anthracene, have robust structures with strong π -conjugated regimes^{17–19}; however, these ORAMs are prone to autooxidation under air-atmosphere conditions due to the extremely oxidation-sensitive

nature of the active centre^{20,27}. Therefore, the current solution for most AOFBs is to operate under inert gas protection conditions, which hinders their practical application.

In this study, we synthesize air-stable naphthalene-based catholytes for AOFBs via a safe and cost-effective approach using a combined chemical and in situ electrochemical process. The dimethylamine decorated naphthalene derivative 2,6,8-trimethylaminemethylene-3,5-dihydroxy-1,4-naphthoquinone (TANQ) exhibits high solubility (~1.5 M) and stable redox-active centres, without obvious capacity decay over 3,000 cycles or 40 days in ambient atmosphere in FBs. Even when an additional air stream is applied, the battery shows excellent stability and is thus not limited by the need for inert gas protection. Furthermore, the synthesis can be scaled up to a kilogramme scale, and a stable stack is assembled, validating the air stability of the naphthalene derivative and the feasibility for practical application.

Results

Naphthalene derivatives for AOFBs

To construct stable and active ORAMs, aromatic hydroxynaphthalene derivatives with a solid framework and high reactivity were selected to obtain a series of water-soluble naphthalene derivatives. During the chemical synthesis process, the hydroxyl group in naphthalene derivatives acted not only as a part of the redox core but also as an activating group to introduce hydrophilic dimethylamine substituents on the aromatic ring through the Mannich reaction. The precursors 2,4,6,8-tetramethylaminemethylene-1,5-naphthalenediol (TAND), 2,6-dimethylaminemethylene-1,5-naphthalenediol (DAND) and 2,4-dimethylaminemethylene-1,5-1-naphthol (DAN) were synthesized, and the corresponding chemical structures were determined from nuclear magnetic resonance (NMR) spectra (Supplementary Figs. 1–6). The final ORAMs TANQ, 2,2',6,6'-tetramethylaminemethylene-5,5'-dihydroxy-1,1'-binaphthoquinone (TADHBQ) and 2-methylaminemethylene-3-hydroxy-1,4-naphthoquinone (AHNQ) were then obtained by in situ electrochemical oxidation in FBs (Fig. 1a), corresponding to their cyclic voltammetry (CV) peaks changed during cycling, as shown in Fig. 1b and Supplementary Figs. 7 and 8. The kinetic constant (k_0) and diffusion coefficient (D) revealed that these naphthalene derivatives could be used as cathode materials for AOFBs (Supplementary Figs. 9–11 and Supplementary Table 1).

Moreover, since the electrochemical oxidation process could be achieved in situ in FBs without further purification, naphthalene derivative precursors (TAND, DAND and DAN) could be used directly in FBs. The charge curves in the first cycle were different from those in the subsequent cycles corresponding to the in situ synthesis steps in FBs (Supplementary Fig. 12a–c), and some open-circuit voltage decreases were attributed to pH changes (Supplementary Fig. 13). Notably, the solubilities of the TADHBQ and AHNQ precursors were greatly improved, as observed by the fact that the electrolyte solution changed from muddy to clear (Supplementary Fig. 14). FBs containing 0.1 M TANQ- and TADHBQ-based catholytes paired with the silicating-stic acid (SWO) anolyte exhibited stable capacities and efficiencies for over 3,000 and 2,000 cycles, respectively, with a Coulombic efficiency (CE) of nearly 100% at a current density of 40 mA cm⁻² (Fig. 1c and Supplementary Figs. 15 and 16). For AHNQ, a decrease in the capacity to only ~89.6% of the original value over 600 cycles was observed (Supplementary Fig. 17); this decrease was potentially due to an unstable half-surrounded structure with two dimethylamines and one hydroxyl anchored on the half ring with no substituents on the other half. Considering the stability and low solubility of the DAND and DAN precursors, the TANQ electrolyte prepared from the TAND precursor was selected for further investigation.

The lifetime of FBs in concentrated electrolytes is vital for their application, and an almost saturated catholyte was used. A high-concentration TANQ-based AOFB with a 1.5 M catholyte also displayed stable cycling performance for 850 cycles (~40 days) with a

capacity of 50 Ah l⁻¹ (Fig. 1d and Supplementary Fig. 12d). The CE was close to 100%, and the average energy efficiency (EE) exceeded 60% during cycling. The slight decrease in the EE was caused by water migration from the anolyte to the catholyte and membrane contamination (Supplementary Fig. 18). A higher capacity was achieved (58 Ah l⁻¹) during the galvanostatic step following potentiostatic charge–discharge at 1.45 V to 0.1 V (Supplementary Figs. 12e and 19). Furthermore, to evaluate the air stability of the naphthalene derivatives, an air stream was continuously pumped into the catholyte during cycling (Fig. 1e,f). Vanadium was selected as the anolyte to pair with naphthalene derivatives because of its higher solubility and better rate performance (Supplementary Figs. 12f and 20). When a 1.0 M TANQ-based catholyte was used, the FB subjected to air bubbling exhibited a stable capacity for ~22 days (>600 cycles with a CE of ~99.4%); this result showed that the air stability of the naphthalene-based catholyte was far superior to those of other reported quinone-based ORAMs¹⁹ (Fig. 1e and Supplementary Fig. 21). No obvious crossover of the naphthalene derivatives was observed during the long-term cycling under air-bubbling conditions (Supplementary Fig. 22). Based on this open-air cycling performance, coupled with the long lifetime of the concentrated naphthalene derivative catholyte, this material has great promise for use in AOFBs. More details regarding the battery performance are provided in Supplementary Note 1 (FB performance).

Electrochemical mechanism

To explore the mechanism of the naphthalene derivatives during the electrochemical process, we employed in situ and ex situ spectroscopic techniques. More than one charge plateau and a higher capacity in the first cycle was observed and attributed to irreversible electrochemical synthesis (Fig. 2a). The structural change from the TAND precursor to TANQ in FBs was investigated by using in situ NMR spectroscopy. The active proton region (8.2 to 10.2 ppm) on the left-hand side of the in situ ¹H NMR spectra and the aromatic proton region (7.1 to 7.7 ppm) on the right-hand side of the spectra changed during the charge–discharge process (Fig. 2a,b), and the corresponding hydrogens were labelled (Fig. 2c). **The overall conversion of TAND to 2,4,6-trimethylaminemethylene-1,5,7,8-tetrahydroxynaphthalene (TATHN) or TANQ could be divided into two stages: irreversible electrochemical oxidation during the first charging (stage 1) and subsequent reversible redox cycling (stage 2).**

During stage 1, the ¹H NMR spectrum of the molecular structure significantly changed. The hydroxyl moiety (H_a) appeared at 8.7 ppm as the battery voltage increased but gradually decreased as electron delocalization of the radicals occurred as a result of the loss of electrons from TAND²⁸ (Fig. 2b). Simultaneously, a broadened hydroxyl moiety (H_c) signal appeared at 8.8 ppm because the pristine trimethylamine group detached from the naphthalene ring owing to the addition of water at the *para* position relative to the hydroxyl group (Fig. 2c); additionally, the corresponding mass change of the molecule was confirmed by liquid chromatography–mass spectrometry (LC–MS) analysis. Moreover, water addition also occurred at the *ortho* position relative to the trimethylamine group, resulting in a second hydroxyl group (H_b) peak at 10.1 ppm. Notably, some very weak signals at 9.1 ppm and 9.4 ppm were observed and then disappeared at the end of the galvanostatic charge process; these signals could be assigned to the active protons of the intermediate resonance structures (TAND-TS, Fig. 2d). The newly appearing H_c and H_b signals were both stable throughout the electrochemical oxidation process. These signals were correlated with each other and exhibited periodic changes in the subsequent discharge/charge cycles; these results indicated the electrochemical reversibility of the new structure, TANQ. (Fig. 2d and Supplementary Fig. 23). In the aromatic proton region of the NMR spectra, the strong H_f signal at ~7.3 ppm (Fig. 2b and Supplementary Fig. 24) split into several weak signals at 7.2 ppm, 7.3 ppm and 7.4 ppm (Fig. 2b) during the charging process; this split was attributed

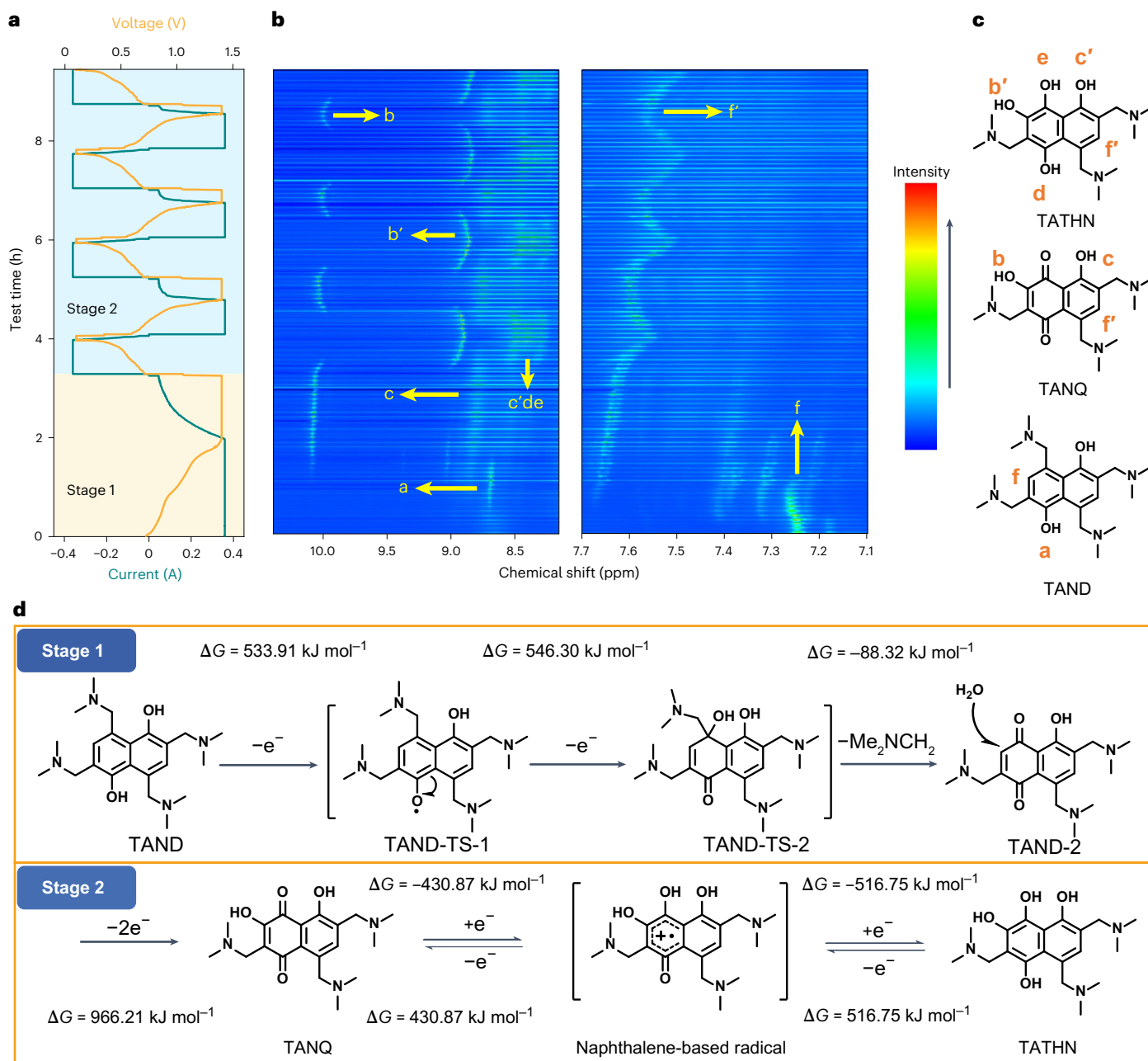


Fig. 2 | In situ NMR of TANQ during electrochemical cycling. **a**, Voltage and current profiles of an FB with 0.2 M TAND as the catholyte and 0.2 M SWO as the anolyte in 1 M H_2SO_4 (including 15% D_2O). **b**, In situ ^1H NMR spectra of the TAND side of the FB during the electrochemical process. **c**, Molecular structures (TAND, oxidized state (TANQ) and reduced state (TATHN)) with the hydrogens

corresponding to peaks in the NMR spectra in **b** labelled. The lowercase letters a, b, b', c, c', d, e, f and f' represent different chemical shifts corresponding to the H in different chemical environments of TAND, TANQ and TATHN. **d**, The electrochemical reaction route from TAND to TATHN and the corresponding Gibbs free energy for each step. TS, transition state.

to the transition state (TAND-TS) mentioned above (Fig. 2d), and these signals gradually decreased during electrochemical oxidation. At almost the same time, a new peak (H_f') corresponding to the addition of a hydroxyl group appeared at a high chemical shift value, and the position of this peak was attributed to the deshielding effect of the electron-deficient structure of the newly generated TANQ molecule. Moreover, the in situ electric field of the electrolyte resulted in a variation in the chemical shift.

After the irreversible electrochemical oxidation stage 1, reversible redox cycling occurred (stage 2; in situ NMR spectra shown in Fig. 2b). TANQ was reduced in the discharge step by accepting electrons and protons (Fig. 2d). The hydroxyl group H_b shifted to a slightly higher

field because of the increase in electron density in the absence of a ketone group. As discharge proceeded at an approximately 50% state of charge, the H_c and H_b signals disappeared, and four hydroxyl signals attributed to the $\text{H}_{b'}$, H_c , H_d and H_e of TATHN appeared at 9 ppm and 8.2–8.6 ppm; however, determining the accurate orientation of each active proton was difficult. A comproportionation reaction occurred between the TANQ and TATHN molecules. The reduced TATHN molecule immediately reacted with TANQ at the initial stage, forming intermediate radicals. After 50% state of charge, a sufficient amount of TANQ was not available to participate in the comproportionation reaction; therefore, the accumulated TATHN was detected. The reverse phenomenon occurred during the next charging process, and these

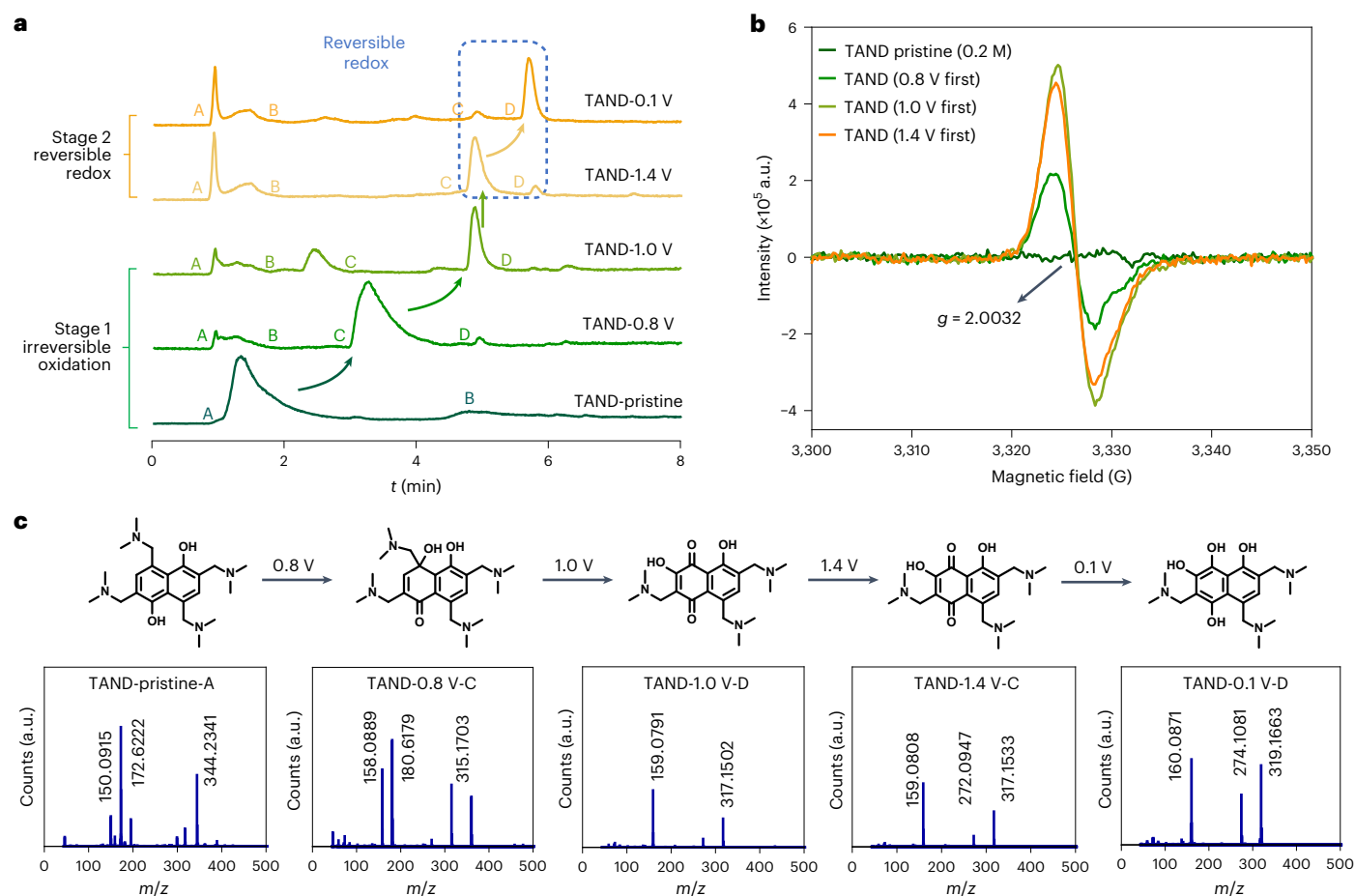


Fig. 3 | LC-MS and EPR spectra of TANQ during operation. **a**, Total ion chromatograms for differently charged TANQ-based electrolytes in an FB investigated by LC-MS analysis. **b**, EPR spectra of radical intermediates during electrochemical oxidation under an air atmosphere. g factor, when $g = 2.0032$, it means a single electron (or a organic free radical) has been detected. **c**, Partial LC-MS spectra of the liquid-phase samples and the corresponding

products at different voltages. TANQ-pristine-A, TANQ-0.8 V-C, TANQ-1.0 V-D, TANQ-1.4 V-C and TANQ-0.1 V-D represent the spectra of peak A for the TANQ-pristine sample, peak C for the TANQ-0.8 V sample, peak D for the TANQ-1.0 V sample, peak C for the TANQ-1.4 V sample and peak D for the TANQ-0.1 V sample, respectively. a.u., arbitrary units.

periodic variations in all the signals reflected the redox process of the in situ synthesized TANQ/TATHN redox couple (Fig. 2b,c).

In addition to in situ NMR spectroscopy, ex situ LC-MS and electron paramagnetic resonance (EPR) spectroscopy were performed to determine the structural changes in the naphthalene derivatives during the electrochemical process (Fig. 3 and Supplementary Fig. 25). As the battery voltage was gradually increased to 0.8 V, 1.0 V and 1.4 V, the observed signals corresponded mainly to TANQ-0.8 V-C, TANQ-1.0 V-D and TANQ-1.4 V-C, respectively (Fig. 3a,c). The spectrum of TANQ-0.8 V-C corresponded to the TANQ-TS-2 transition state. TANQ-1.0 V-D was the product obtained after the addition of water to the isomers of TANQ-0.8 V-C, which possessed a new hydroxyl moiety at the β -carbon position of the pristine molecule. The spectra of TANQ-1.4 V-C and TANQ-0.1 V-D were assigned as TANQ and the reduced state TATHN. The TANQ and TATHN underwent a reversible transformation during the cell charge-discharge process (Figs. 2d and 3c). Moreover, the EPR response intensity significantly increased during the initial charging process, indicating the formation of naphthalene-based radicals (TANQ-TS-1, Fig. 3b). When a cutoff voltage of 1.4 V was reached, a notable decrease in the EPR intensity was observed, which indicated that most of the radical intermediate, TANQ-TS-1, had been converted into TANQ (Fig. 2d).

The precursors of TADHBQ, AHNQ, DAND and DAN have only two dimethylamine groups and one or two hydroxyl groups substituted on

the naphthalene ring (Fig. 1a). DAND underwent dimerization (Supplementary Figs. 26 and 27), and DAN contained some oligomers during the in situ electrochemical oxidation process (Supplementary Figs. 28–30).

Structural stability

Density functional theory (DFT) calculations were used to explore the structure-stability relationships of the naphthalene derivatives. Compared with previously reported quinone derivatives, the as-prepared naphthalene molecules in this study exhibited much better antioxidation ability, especially under an air atmosphere²⁹. Structural stability, particularly for a radical intermediate, is important for the development of stable redox reactions of the naphthalene derivatives. **The simulated electron spin distribution reveals that the main single electron delocalization regions of the radical are either occupied by bulky side chain substituents or surrounded (Supplementary Fig. 31); this inhibits potential attack by other active species (for example, water and oxygen species) and results in excellent stability.**

In addition to the radical stability, a potential H_2O attack on the conjugated α,β -ketone is another explanation for the loss of redox activity (Supplementary Fig. 32). DFT calculations of the hydroxyl-containing TANQ structure show that the Gibbs free energy of water attack at this occupied site ($\Delta G = 267.47 \text{ kJ mol}^{-1}$) is much greater than that of water attack at the unsubstituted β -carbon position mentioned above

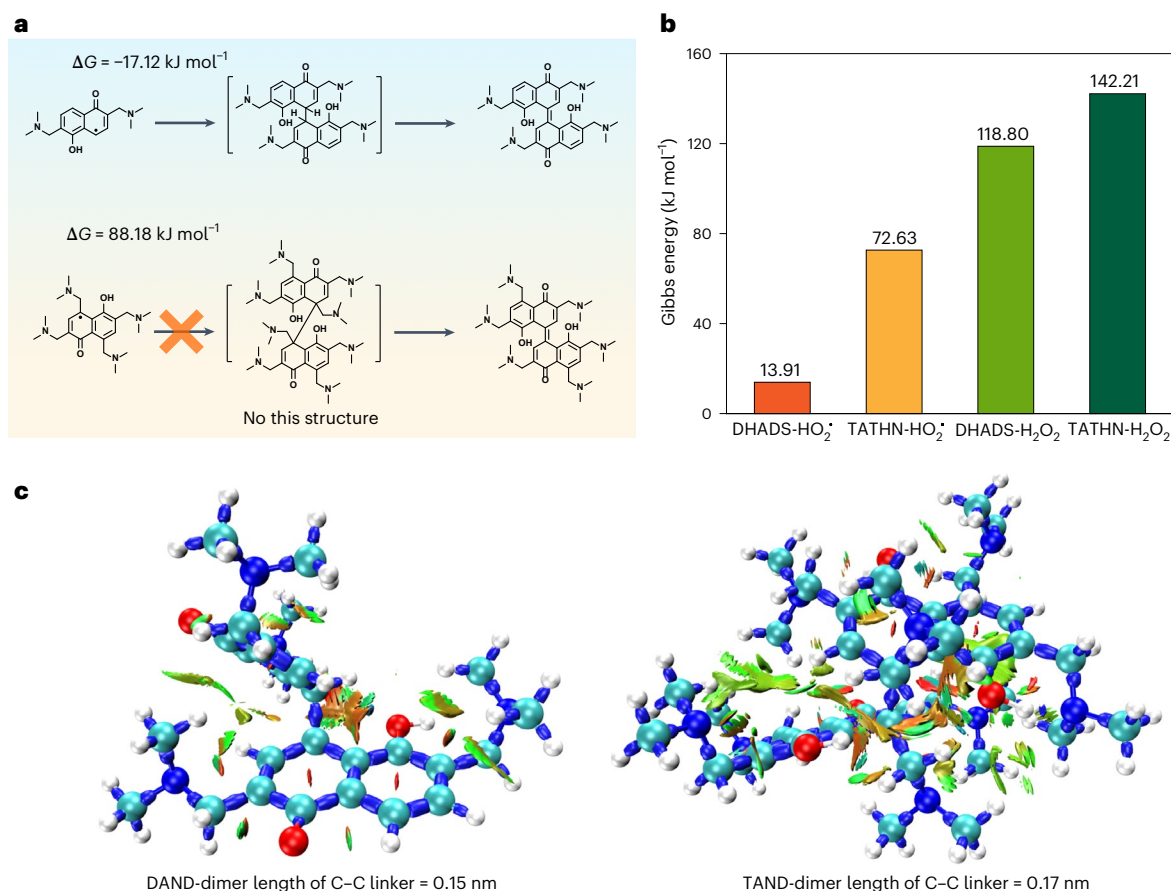


Fig. 4 | Stable radical intermediates and mechanism. a, Proposed dimerization of DAND to form TADHBQ and an assumed dimerization process for the TAND derivative. The dimer of TAND does not exist confirmed by calculation as its chemical bond is out of general covalent bond range. **b**, Gibbs energies for RAM oxidation reactions with oxygen species (DHADS, the reduced state of AQDS). **c**, IRI showing the surface map of two kinds of dimers with different

configurations: the structure on the left is the DAND dimer and the structure on the right is the TAND dimer. The red, green, blue and white balls represent the oxygen, carbon, nitrogen and hydrogen atoms, respectively. The blue bars and regions bridging the atoms represent chemical bonds. The green region represents the Van der Waals force (vdW). The red region represents repulsion.

($\Delta G = -88.32 \text{ kJ mol}^{-1}$) (Fig. 2d); these results indicate that the Michael reaction is difficult at an occupied β -carbon site, which further confirms the stability of the multi-substituted naphthalene.

The polymerization of the TAND molecule, whose naphthalene rings are nearly saturated with substituents, is effectively inhibited; however, polymerization of the DAND and DAN molecules, which contain fewer substituents, still occurs. The calculated Gibbs free energies of the proposed TAND dimerization reactions indicated that the polymerization of TAND was not possible (Fig. 4a). Additionally, the proposed dimerization during the TAND oxidation process was not possible owing to interaction region indicator (IRI) simulation; here the proposed dimer possessed a large amount and considerable variety of molecular interactions (van der Waals interactions) and steric hindrance (Fig. 4c and Supplementary Fig. 33)³⁰, and the C-C bond length of the proposed TAND dimer was 0.17 nm, exceeding the normal length of a typical C-C bond (0.15 nm).

Compared with 9,10-dihydroxyanthracene-2,7-disulfonate (DHADS), the naphthalene derivatives are only slightly disturbed and specifically involve irreversible oxygen-driven side reactions and oxidation of the reduced states under continuous airflow conditions (Supplementary Figs. 34–37). The reduced states (TATHN, TATHBN and ATHN) cannot be completely oxidized while DHADS is oxidized to anthraquinone-2, 6-disulfonate (AQDS) by continuous air bubbling (Supplementary Table 2); these results may be attributed to the narrower potential gap between the O_2 reduction reaction

($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$ (2e^- pathway, 0.695 V versus standard hydrogen electrode, pH 0) and the oxidation of the reduced state of naphthalene derivatives than that of AQDS (0.485 V for TANQ versus 0.205 V for AQDS). A simulation of possible side reactions between RAMs and oxidative oxygen species (H_2O_2 and peroxide radicals) is proposed, and the theoretical calculation results show that TANQ exhibits greater energy and resistance to oxidation than DHADS (Fig. 4b and Supplementary Fig. 38). In general, this air stability can be attributed to the following factors: (1) Some alkyl spacers are present between the amino groups and the aromatic ring, which weakens the negative inductive effect of the protonated tertiary amines. (2) Multiple substituents as scaffolds provide steric effects to inhibit the side reactions and improve ORAM stability. (3) Protonated water at relatively low pH is a weaker nucleophile than the OH^- species. Air stability is one part of the molecular stability and is a comprehensive indicator used to evaluate the tolerance of molecules to potential side reactions, which involves numerous influencing factors (Supplementary Note 2, 'Molecular stability').

Scaled-up production and pilot stack

To further test the practicality of the developed naphthalene derivatives, TAND synthesis was scaled up to the kilogramme scale and pilot-scale battery stacks were prepared; this was possible because of the simple synthesis process and stable molecular structure (Supplementary Fig. 39). As shown in Fig. 5a, 5 kg of TAND was obtained by using a one-pot reaction in a 20 l reactor (94% yield, Supplementary

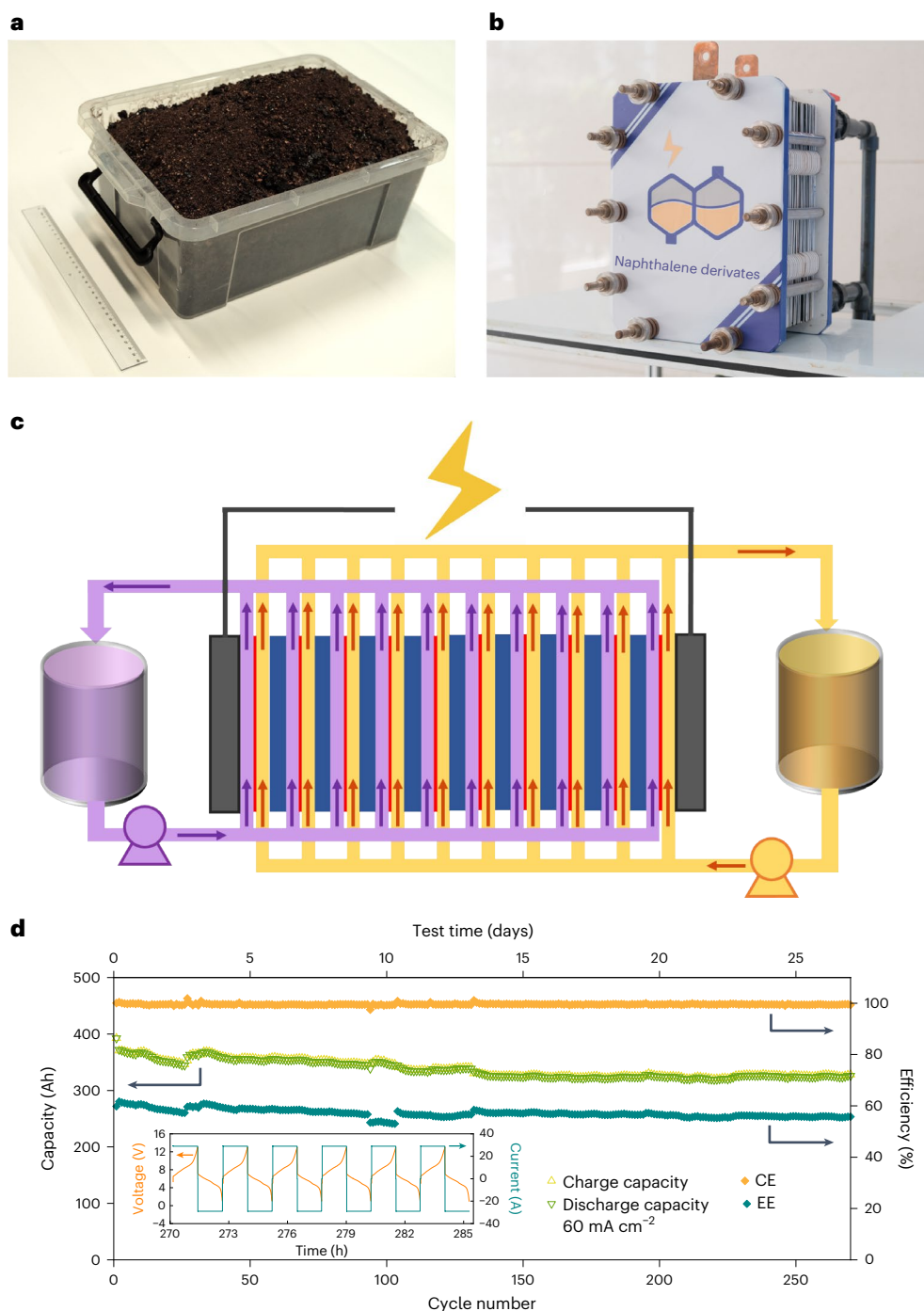


Fig. 5 | Scaled-up TAND synthesis and pilot stacks. **a, b**, Digital photographs of the kilogramme-scale TANQ precursor TAND (**a**, total of 10 kg in the box) and a pilot-scale AOFB stack (**b**). **c**, Schematic diagram of a flow stack with a TANQ

catholyte and a vanadium anolyte. **d**, The system capacity and efficiencies of the pilot-scale stack based on a 0.6 M TANQ-based catholyte and 1.0 M vanadium anolyte (inset, corresponding charge–discharge profiles).

Fig. 40). The cost analysis and calculation of the raw materials indicated that the cost of TAND is quite competitive, at only US\$3.6 per kg (US\$54.1 per kWh) (Supplementary Table 3). TANQ also shows a cost-competitive advantage from a technoeconomic analysis (US\$32.7 per kWh, Supplementary Fig. 41 and Supplementary Table 4). Owing to the mild reaction conditions and simple post-treatment, future commercialization of this product is feasible. Ten units of 476 cm² stacks with a 0.15 M or 0.6 M TAND precursor catholyte and a vanadium anolyte (0.5 M and 1 M) were assembled (Fig. 5b,c). The stack containing the 0.15 M TAND catholyte delivered an incremental system discharge capacity of 91 Ah with CE and EE values of 98% and 72%, respectively,

at a current density of 40 mA cm⁻² (Supplementary Fig. 42). When a current density of 60 mA cm⁻² was reached, a higher CE of 99% and an average EE of 64% were obtained, accompanied by an average discharge capacity of 91 Ah. Notably, almost no capacity decay was observed over 500 cycles; these results showed the high stability of the naphthalene derivative catholyte in the stack. EE decay during cycling was observed and was mainly caused by the polarization originating from solvent migration. Moreover, upon increasing the catholyte concentration to 0.6 M, a higher system capacity of ~372 Ah was obtained, with an average discharge capacity of approximately 330 Ah and a capacity retention of 99.95% per cycle over 270 cycles (~27 days) (Fig. 5d). A capacity decay at

approximately 90 to 100 cycles caused by the oxidation of vanadium(II) was recovered after the addition of the vanadium anolyte. The stack performance under an air atmosphere was sufficiently stable to consider TAND a catholyte candidate. Owing to the combination of one-pot chemical synthesis and in situ electrochemical oxidation in AOFBs, the efficient preparation of kilogramme-scale ORAMs without complicated purification can effectively be performed, and this strategy is expected to be applied in other sustainable ORAM designs in the future.

Discussion

We have prepared scalable, stable and air-insensitive naphthalene derivative catholytes by using a combined strategy of regular chemical synthesis and in situ electrochemical processes. The in situ electrochemical process begins with the oxidation of active hydroxyl groups followed by the addition of water, and a kilogramme-scale molecule is successfully produced and evaluated in an FB stack. Furthermore, sulfo group-decorated naphthalene molecules with increased redox potential and low cost can be obtained accordingly (Supplementary Figs. 43 and 44). ORAMs are designed from sustainable and green-economic perspectives, and this facile, scalable and cost-effective approach is also suitable for aromatic compounds containing active hydroxyl groups, such as naphthalene, anthracene and pyrene derivatives; thus, this study can be used to facilitate a new field of air-insensitive ORAM design strategies for sustainable electrochemical energy storage.

Methods

Chemicals

For this study, 1,5-dihydroxynaphthalene (97%), 1-naphthol (98%), a dimethylamine solution (37% in water) and a formaldehyde solution (40% in water) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Tungstosilicic acid hydrate (SWO, Analytical Reagent), ethanol (Analytical Reagent), dimethylsulfoxide- d_6 (99.8 at. % D) and D_2O (99.9 at. % D) were purchased from Beijing Innochem Science & Technology Co., Ltd.

Instruments

In this work, the 1H NMR, ^{13}C NMR and in situ NMR spectra were measured on a Bruker 400 M NMR (AVANCE III 400 MHz) spectrometer. Ultraviolet–visible spectra were collected on an ultraviolet–visible spectrophotometer (TU-1901) from PERSEE, and Fourier-transform infrared spectra were conducted on a Thermo Scientific Nicolet iS 50 spectrometer. LC–MS data were acquired with an Agilent Q-TOF 6540 instrument. EPR spectroscopy was performed by means of a Bruker A200 instrument. Electrochemical measurements involving CV and linear sweep voltammetry were recorded by means of a Gamry Reference 1000/3000 instrument. The battery test of in situ NMR was conducted by a CT-4008, NEWARE Battery Testing System. Single battery and stack performance were assessed with Arbin Instruments LBT21084HC (5 V, 20 A) and BT2000 (50 V, 200 A), respectively.

Synthesis of TAND

The compound 1,5-dihydroxynaphthalene (3.2 g, 0.02 mol) was first dissolved in 50 ml ethanol in a 200 ml thick-walled pressure bottle in an ice bath, and then formaldehyde solution (5.0 equiv., 37%) and an aqueous solution of dimethylamine (5.0 equiv., 40%) were added to the flask in succession. The bottle was sealed and put into an oil bath, and the mixture was reacted at 60 °C for 6 h with stirring. After the excess formaldehyde, dimethylamine and solvent were evaporated, a brown solid was obtained. The brown solid was further dried under vacuum at 60 °C for 10 h (7.4 g, yield 95%).

Synthesis of DAND

The compound 1,5-dihydroxynaphthalene (3.2 g, 0.02 mol) was first dissolved in 50 ml ethanol in a 200 ml thick-walled pressure bottle in an ice bath, and then formaldehyde solution (2.2 equiv., 37%) and an aqueous

solution of dimethylamine (2.2 equiv., 40%) were added into the flask in succession. Then, the mixture was reacted in a sealed bottle at room temperature for 1 h under stirring. The obtained solid was filtered and subsequently washed with ethanol. The grey solid that was obtained was further dried under vacuum at 60 °C for 10 h (4.4 g, yield 82%).

Synthesis of DAN

The compound 1-naphthol (2.88 g, 0.02 mol) was first dissolved in 50 ml ethanol in a 200 ml thick-walled pressure bottle in an ice bath, and then formaldehyde solution (3.0 equiv., 37%) and an aqueous solution of dimethylamine (3.0 equiv., 40%) were added into the flask in succession. Then, the mixture was reacted in a sealed bottle at 20 °C for 24 h under stirring. The obtained solid was filtered and subsequently washed with ethanol. The orange solid that was obtained was further dried under vacuum at 60 °C for 10 h (3.2 g, yield 62%).

Synthesis of TAND

The compound 1,5-dihydroxynaphthalene (2.24 kg, 12 mol) was first dissolved in 8 l ethanol in a 20 l stainless steel reactor, and then a formaldehyde solution (4.4 equiv., 37%) and an aqueous solution of dimethylamine (4.4 equiv., 40%) were added to the reactor with stirring. Attention must be given to the fact that formaldehyde and dimethylamine solution must not be added too quickly, as the reaction will quickly produce heat when expanding the raw materials. The mixture was reacted at 70 °C for 15 h under stirring in a stainless reactor. After the excess formaldehyde, dimethylamine and solvent were evaporated, a brown solid was obtained. This brown solid was further dried under vacuum at 70 °C for 24 h (5.1 kg, yield 94%).

Characterizations

The concentration of each naphthalene derivative used for electrochemical measurements was 10 mM. In the CV study, a graphite plate was used as the working and counter electrodes and Ag/AgCl was used as the reference electrode. The CV test was conducted at a sweeping rate of 50 mV^{−1}. In the rotating disk electrode (RDE) test, a graphite RDE was used as the working electrode, a graphite plate was used as the counter electrode and Ag/AgCl was used as the reference electrode. The RDE test was conducted in the potential range of 0.0 to 0.8 V (versus Ag/AgCl), and the rotation rates were 400, 625, 900, 1,225, 1,600, 2,025 and 2,500 rpm. The diffusion coefficient (D) in 3 M H₂SO₄ solution was calculated according to the Levich equation:

$$i = 0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C \quad (1)$$

where i is the limiting current, n is the electron transfer number, F is the Faraday constant (96,485 C mol^{−1}), A is the surface area of the working electrode, D is the diffusion coefficient, ω is the angular velocity in rad s^{−1}, ν is the kinetic viscosity (1.55 × 10^{−2} cm² s^{−1} in a 3 M H₂SO₄ solution) and C is the molar concentration of the ORAMs.

The kinetic constant (k_0) was calculated according to the Butler–Volmer equation:

$$i_0 = nFCk_0 \quad (2)$$

where i_0 is the exchange current, which can be determined by fitting i_k (kinetic current) to the Tafel plot when the overpotential is equal to zero according to the Koutecky–Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C} \quad (3)$$

Battery performance

Each FB was composed of poly(tetrafluoroethylene) frames, graphite plates (current collector), graphite felts (electrode) with an active area

of 9 cm² (for ATHN-based FBs) or 48 cm² (for TANQ- and TADHBQ-based FBs) and a homemade polybenzimidazole ion-conducting membrane³¹. The electrolyte was pumped through a peristaltic pump and the air was pumped by an external air pump (air-bubbling test). For the long-term cycling test of TANQ, a 0.1 to 1.5 M TANQ-based catholyte and a 0.1 to 0.3 M SWO anolyte were used in the FBs. For the 1.0 M TANQ-based FB (air-bubbling test and rate performance), a 1.0 M TANQ-based catholyte and a 1 M vanadium anolyte were used. For the long-term cycling test of TADHBQ, a 0.1 M TADHBQ-based catholyte and a 0.1 M SWO anolyte were used in the FBs. For the long-term cycling test of ATHN, a 0.05 M ATHN-based catholyte and a 0.1 M SWO anolyte were used in the FBs. For the flow stacks, 10 units of 476 cm² stacks with a 0.15 M and 0.6 M TAND precursor catholyte and a vanadium anolyte (0.5 M and 1 M) were used.

In situ NMR

For in situ NMR, 0.2 M TAND was used as the catholyte and 0.2 M SWO was used as the anolyte in 1 M H₂SO₄ (including 15% D₂O). The electrolyte was pumped through a peristaltic pump, while the cathode flowed through a tailored NMR tube for detection. The battery progress was conducted at a galvanostatic stage of 0.36 A (40 mA cm⁻²) followed by a potentiostatic charge-discharge at 1.4 V to 0.1 V (0.045 A limited current, 5 mA cm⁻²).

LC-MS

Naphthalene derivatives (0.05 M) in 3 M H₂SO₄ were used for the electrochemical process, and the corresponding electrolytes at different states were diluted 50 times with ultrapure water and analysed via LC-MS.

EPR

Naphthalene derivatives (0.1 M) in 3 M H₂SO₄ were used in the electrochemical process, and the corresponding electrolytes at different states were analysed via EPR under air-atmosphere conditions. All samples were exposed to air for more than 24 h before the EPR test.

Computational methods

DFT calculations were performed with the Gaussian v.16 (ref. 32) package. The B3LYP hybrid functional with 6-31G* level of basis set including the atom-pairwise dispersion (D3) correction³³ with Becke–Johnson damping was applied for geometry optimization. Each optimized structure was subsequently analysed by harmonic vibration frequencies at the same level. The transition state structures were checked by harmonic vibrational frequencies to ensure that they were on the saddle point of the potential energy surface, which were identified by the presence of a single imaginary frequency corresponding to the reaction mode. The solvation free energy was calculated by the energy calculated from an implicit universal water solvation model based on solute electron density³⁴ subtraction that was calculated from the gas phase with an M052X/6-31G*(D3) calculation level. A 1.89 kcal mol⁻¹ was added as the correction of solvation free energy from 1 atm in gas phase to 1 mol⁻¹ solution. A single-point energy calculation of each optimized structure was carried out using B3LYP/def2-TZVP³⁵ including the D3(Becke–Johnson) correction. The Gibbs free energy of each structure was the sum of the thermal correction to the Gibbs free energy from the frequency calculation by the Shermo package, the solvation free energy and the single-point energy. The IRI³⁰ was analysed by the Multiwfn³⁶ package and drawn by the VMD³⁷ package.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

All data generated and/or analysed from this study are available from the corresponding authors upon reasonable request. Source data are provided with this paper.

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Author contributions

Z.Z. and C.Z. conceived the idea and designed the experiments. C.Z., S.L. and X.L. supervised the project. Z.Z. conducted the experiments and data analysis. M.Z. and C.Z. helped with battery performance tests. T.L. contributed to the DFT simulation. Z.Z., T.L., C.Z. and X.L. organized and wrote the manuscript. All authors contributed to the discussion and revision of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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